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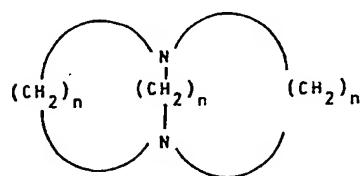
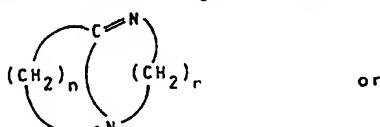
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(54) A process for rapidly curing a brominated fluoroelastomer.

(57) A process for rapidly curing a fluoroelastomer which comprises mixing and heating a fluoroelastomer copolymer whose interpolymerized units consist essentially of vinylidene fluoride, at least one other fluorine-containing monomer copolymerizable therewith, said monomer being a compound which contains 2-7 carbon atoms, contains no bromine, and contains at least as many fluorine atoms as carbon atoms and contains up to 3 mole percent of units derived from a bromine-containing olefin; a quaternary phosphonium compound; a bisphenol or an ammonium or phosphonium salt thereof; and a dialkylaminopyridine or a diazabicyclo compound having the formula

where n is 2-8 or

0.2-0.8 parts by weight per hundred parts fluoroelastomer of a carboxylic acid salt of (a) or (b).



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TITLE

A PROCESS FOR RAPIDLY CURING A

BROMINATED FLUOROELASTOMER

BACKGROUND OF THE INVENTION

5 This invention is directed to a process for rapidly curing a fluoroelastomer that contains units derived from a brominated olefin.

Fluoroelastomers that contain units derived from brominated olefins have been favorably accepted
10 by the industry. These fluoroelastomers are peroxide-curable and the cured products have good resistance to damage by heat, solvents and corrosive chemicals. Such fluoroelastomers containing units derived from brominated olefins can also be cured
15 with quaternary phosphonium compounds and bisphenols. This is advantageous because of the improved milling behavior and mold release characteristics of this cure system as compared to a peroxide cure system. However, the cure times are
20 excessively long and can be as much as about 20 minutes. Such long cure times are uneconomical because of the limitation on equipment available to the manufacturer. The present invention describes a process in which compositions of fluoroelastomer
25 containing units derived from a brominated olefin are readily processible, do not stick to the mold and, most importantly, have fast cure times while still showing excellent physical properties.

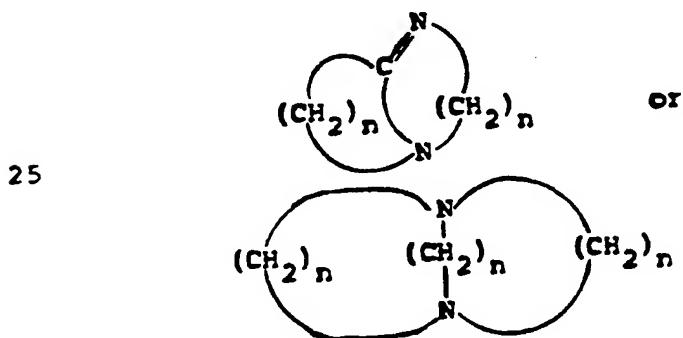
SUMMARY OF THE INVENTION

30 The present invention is directed to a process for rapidly curing a fluoroelastomer composition which comprises mixing and heating:

(1) a fluoroelastomer copolymer whose interpolymerized units consist essentially of (a)

AD-5353 35 vinylidene fluoride, (b) at least one other

- fluorine-containing monomer copolymerizable therewith, said monomer being a compound which contains 2-7 carbon atoms, contains no bromine atoms, and contains at least as many fluorine atoms as 5 carbon atoms and (c) contains up to 3 mole percent of units derived from a bromine-containing olefin with the proviso that enough of such units are present to provide at least 0.05 weight percent bromine in the copolymer;
- 10 (2) a vulcanization accelerator that is a quaternary phosphonium compound;
- (3) a cross-linking agent selected from the group consisting of bisphenols or an ammonium or phosphonium salt thereof;
- 15 the improvement which comprises adding to the composition 0.1-0.4 parts by weight per hundred parts fluoraelastomer of (a) a dialkylaminopyridine wherein the alkyl groups independently contain 1-5 carbon atoms or (b) a diazabicyclo compound of the formula



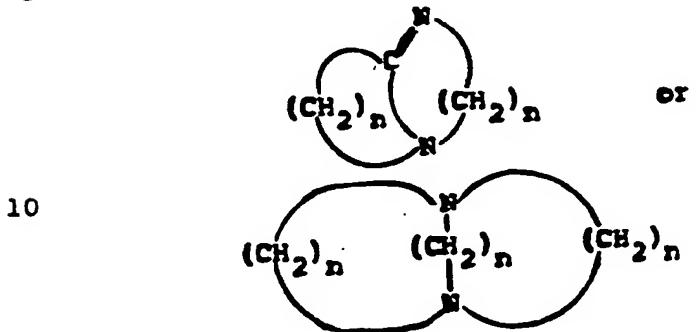
30 where n is 2-8 or 0.2-0.8 parts by weight per hundred parts fluoraelastomer of a carboxylic acid salt of (a) or (b).

DESCRIPTION OF THE PREFERRED EMBODIMENTS

35 The fluoraelastomer compositions contain 0.1-0.4 parts by weight, preferably 0.12-0.2 parts by

weight, per hundred parts fluoroclastomer of (a) a dialkylaminopyridine wherein the alkyl groups independently contain 1-5 carbon atoms or (b) a diazabicyclo compound of the formula

5



where n is 2-8 or

15 0.2-0.8 parts per hundred parts

fluoroclastomer of a carboxylic acid salt of (a) or (b). Representative diazabicyclo compounds include 1,5-diazabicyclo[4.3.0]non-5-ene, 1,4-diazabicyclo[2.2.2]octane, 1,8-diazabicyclo[5.4.0] undec-7-ene and carboxylic acid salts of these compounds, said carboxylic acids usually containing from 6-20 carbon atoms, for example, octanoic acid, dodecanoic acid and hexanoic acid. Representative dialkylaminopyridines include 20 p-dimethylaminopyridine, dipropylaminopyridine and carboxylic acid salts thereof, said carboxylic acids usually containing 6-20 carbon atoms.

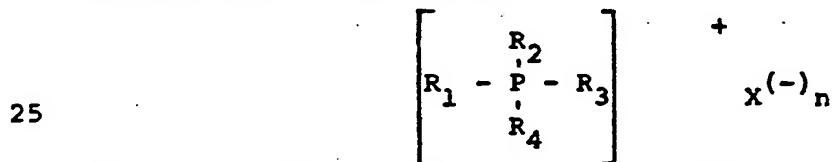
25 The fluoroclastomer contains units derived from vinylidene fluoride. In addition to units of vinylidene fluoride, the fluoroclastomer copolymer contains units derived from at least one other fluorine-containing monomer copolymerizable with vinylidene fluoride, said monomer being a compound which contains 2-7 carbon atoms, contains no bromine atoms, and contains at least as many fluorine atoms

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as carbon atoms. Representative monomers include hexafluoropropylene, pentafluoropropylene, tetrafluoroethylene and perfluoroalkylperfluorovinyl ether where the alkyl group contains 1-5 carbon atoms. Preferred combinations of fluoroelastomers include units from any one of the following two combinations: vinylidene fluoride and hexafluoropropylene or pentafluoropropylene and tetrafluoroethylene or vinylidene fluoride, 10 tetrafluoroethylene and perfluoromethylperfluorovinyl ether. The fluoroelastomers that are generally used in this process and cure under ordinary conditions rather slowly are fluoroelastomers containing at least about 30% by weight vinylidene fluoride units. 15 Usually such fluoroelastomers contain about 30-60 weight percent vinylidene fluoride units, about 20-50 weight percent hexafluoropropylene units or pentafluoropropylene or perfluoromethyl perfluorovinyl ether units and about 3-35 weight percent tetrafluoroethylene units. The fluoroelastomers used in the process also contain units derived from a bromine-containing olefin. The term "bromine-containing olefin" as used herein means an olefin in which at least one hydrogen atom has 20 been replaced with a bromine atom, and optionally one or more of the remaining hydrogen atoms have been replaced with an atom of another halogen, preferably fluorine. Some compounds of this type are available commercially and others can be prepared by methods 25 known in the art, for example as shown by Tarrant and Tandon, 34 J. Org. Chem. 864 (1969) and by Fainberg and Miller, JACS 4170 (1957). Representative bromine-containing olefins which are copolymerizable with the monomers used to form the copolymer include 30 35 bromotrifluoroethyl ne,

4-bromo-3,3,4,4-tetrafluorobutene-1, vinyl bromide,
 1-bromo-2,2-difluoroethylene, perfluoroallylbromide,
 4-bromo-1,1,2-trifluorobutene,
 4-bromo-1,1,3,3,4,4-hexafluorobutene,
 5 4-bromo-3-chloro-1,1,3,4,4-pentafluorobutene,
 6-bromo-5,5,6,6-tetrafluorohexene,
 4-bromo-perfluorobutene-1, and
 3,3-difluoroallylbromide. It is preferable to use
 sufficient units of the brominated olefin to provide
 10 about 0.3-1.5 weight percent bromine in the
 fluoroelastomer copolymer. Bromine-containing
 fluoroelastomers used in the process of this
 invention are further described in U.S. Patent
 4,214,060, the disclosure of which is incorporated
 15 herein by reference.

The vulcanization accelerators used in the
 process of this invention are quaternary phosphonium
 compounds. These compounds are usually added in
 amounts of from about 0.6-2 parts by weight per
 20 hundred parts fluoroelastomer, preferably 1-1.3 parts
 by weight. The phosphonium compounds can be
 represented by the formula



25 where P is phosphorous; R₁, R₂, R₃ and R₄ are
 selected individually from the group alkyl, aryl,
 aralkyl and alkenyl usually containing 1-20 carbon
 atoms, and the chlorine, fluorine, bromine, cyano,
 30 -OR, and -COOR substituted analogs thereof, R being
 selected from the group C₁-C₂₀ alkyl, aryl,
 aralkyl and alkenyl; X is a halide, especially
 chloride, sulfate, sulfite, bisulfite, carbonate,
 nitrate, pentachlorothiophenolate, tetrafluoroborate,
 35

hexafluorosilicate, hexafluorophosphat , dimethyl phosphate, a C₁-C₂₀ alkyl-, aryl-, aralkyl-, and alkenyl-/carboxylate and dicarboxylate; n is 1 or 2 and equal to the valance of anion X. These compounds are described in Pattison U.S. Patent 3,876,654.

- Particularly preferred accelerators are benzyl triphenyl phosphonium chloride and -bromide and phenolates of 4,4'-hexafluoroisopropylidene diphenol. Other useful accelerators include the following: methyl trioctyl phosphonium tetrafluoroborate, methallyl tributyl phosphonium chloride or- bromide, tetraphenyl phosphonium bromide and -chloride, benzyl trioctyl phosphonium bromide and -chloride, benzyl tributyl phosphonium bromide and- chloride, methyl trioctyl phosphonium acetate, methyl trioctyl phosphonium chloride, methoxyethoxyethyl trioctyl phosphonium chloride, tetraoctyl phosphonium bromide, butyl trioctyl phosphonium bromide, 1-carbethoxyethyl triphenyl phosphonium chloride, tetrabutyl phosphonium chloride, 2,4-dichlorobenzyl triphenyl phosphonium chloride, m-trifluoromethylbenzyl trioctyl phosphonium chloride, 2,2,3,3-tetrafluoropropyl trioctyl phosphonium chloride;
- 2,2,3,3,4,4,5,5-octafluoropentyl trioctyl phosphonium chloride, isobutyl triphenyl phosphonium bromide, 2-pentyl triphenyl phosphonium bromide, 4-methylbenzyl triphenyl phosphonium chloride, 4-chlorobenzyl triphenyl phosphonium chloride,
- diphenylmethyl triphenyl phosphonium chloride, m-trifluoromethylbenzyl triphenyl phosphonium chloride, 1-naphthylmethyl triphenyl phosphonium chloride, 2-cyanobenzyl triphenyl phosphonium bromide, 4-cyanobutyl triphenyl phosphonium bromide,
- a-carbethoxybenzyl triphenyl phosphonium bromide,

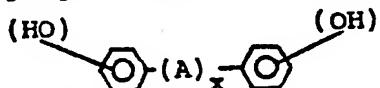
carbethoxym thyl triphenyl phosphonium bromid ,
methoxymethyl triphenyl phosphonium chloride,
allyloxymethyl triphenyl phosphonium chloride, allyl
triphenyl phosphonium chloride, methallyl triphenyl
5 phosphonium chloride and- bromide, and tetrabutyl
phosphonium bromide.

A typical component accelerator, such as
benzyl trioctyl phosphonium chloride, can be prepared
by (1) providing a mixture of 37.0 grams trioctyl
10 phosphine, 25.2 grams benzyl chloride, and 20 ml.
methanol; (2) heating the mixture under nitrogen at
84°-90°C. under reflux for 11 hours; (3) removing
methanol and unreacted benzyl chloride by
distillation with 100 ml. of water; (4) removing
15 water by means of a separatory funnel; (5) drying the
resulting crude product (benzyl trioctyl phosphonium
chloride) by exposing it to dry air in a laboratory
hood for 16 hours at 25°C. and then heating it for 4
hours at 55°C. under a subatmospheric pressure of
20 about 2 mm. of mercury. The preparation of
phosphonium compounds useful as the accelerators are
described by Davies and Lewis in J. Chem. Soc. 1934,
1959, and by Henderson and Buckler in J. Am. Chem.
Soc. 82, 5794 (1960).

25 Before the accelerator is blended with the
other ingredients of the composition, it is often
desirable to combine it (e.g., by mixing in a mortar
and pestle) with fine particles of a solid material
that undergoes no harmful reaction with the
30 accelerator. For example, it can be combined in
adsorbed or absorbed relationship with finely divided
calcium carbonate, calcium silicate, silica or the
like to form composite accelerator particles.

The cross-linking agent of the novel curable
35 composition is selected from known polyhydroxylic

aromatic compounds capable of functioning as a cross-linking agent for the elastomeric copolymer. The cross-linking agent is usually added in amounts of from about 1.5-4 parts by weight per hundred parts fluoroelastomer, preferably 2-3 parts by weight. The cross-linking agent can be a bisphenol of the formula



- wherein A is a difunctional aliphatic, cycloaliphatic, or aromatic radical of 1-13 carbon atoms, or a thio, oxy, carbonyl, sulfinyl, or sulfonyl radical; A is optionally substituted with at least one chlorine or fluorine atom; x is 0 or 1; and the aromatic ring of the bisphenol is optionally substituted with at least one atom of chlorine, fluorine, or bromine, a -CHO group, or a carboxyl or acyl radical (e.g., a -COR where R is OH or a $\text{C}_1\text{-}\text{C}_8$ alkyl, aryl, or cycloalkyl group). It will be understood from the above bisphenol formula that the -OH groups can be attached in any position (other than number one) in either ring. Blends of two or more such compounds can also be used.

Referring to the bisphenol formula shown in the previous paragraph, when A is alkylene, it can be for example methylene, ethylene, chloroethylene, fluoroethylene, difluoroethylene, 1,3-propylene, 1,2-propylene, tetramethylene, chlorotetramethylene, fluorotetramethylene, trifluorotetramethylene, 2-methyl-1,3-propylene, 2-methyl-1,2-propylene, pentamethylene, pentachloropentamethylene, pentafluoropentamethylene, and hexamethylene. When A is alkylidene, it can be for example ethylidene, dichloroethylidene, difluoroethylidene, propylidene, isopropylidene, trifluoroisopropylidene, hexafluoroisopropylidene, butylidene,

heptachlorobutylidene, heptafluorobutylidene, pentylidene, hexylidene, and 1,1-cyclohexylidene.

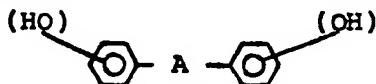
When A is a cycloalkylene radical, it can be for example 1,4-cyclohexylene,

- 5 2-chloro-1,4-cyclohexylene,
2-fluoro-1,4-cyclohexylene, 1,3-cyclohexylene,
cyclopentylene, chlorocyclopentylene,
fluorocyclopentylene, and cycloheptylene.

Furthermore, A can be an arylene radical such as

- 10 m-phenylene, p-phenylene, 2-chloro-1,4-phenylene,
2-fluoro-1,4-phenylene, o-phenylene, methylphenylene,
dimethylphenylene, trimethylphenylene,
tetramethylphenylene, 1,4-naphthylene,
3-fluoro-1,4-naphthylene, 5-chloro-1,4-naphthylene,
15 1,5-naphthylene, and 2,6-naphthylene.

- In a preferred composition of the present invention for the manufacture of cured articles having especially good properties the accelerator used is an alkyl- or aralkyl-triarylphosphonium compound, and the crosslinking agent used is a bisphenol having the formula



wherein A is an electron-withdrawing group.

- 25 In the highly preferred composition described in the previous paragraph, the electron-withdrawing group A of the bisphenol formula is preferably carbonyl, sulfinyl, sulfonyl, perfluorinated alkylene or perfluorinated alkylidene. The accelerator is preferably benzyl triphenyl phosphonium chloride or benzyl triphenyl phosphonium bromide. The cross-linking agent is preferably a compound having an oxidation potential of about 1.6-2.2 volts. The oxidation potential of
30 the cross-linking agent can be conveniently measured

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in the manner described in G. E. Penketh in "J. Appl. Chem." Vol. 7, page 512 (1957) except using acetonitrile as the solvent and using 0.1 molar tetramethyl ammonium perchlorate as the supporting

5 electrolyte.

One highly preferred cross-linking agent is hexafluoroisopropylidene -bis(4-hydroxybenzene), which has an oxidation potential of 2.07 volts. A second preferred cross-linking agent is 10 4,4'-dihydroxydiphenyl sulfone, which has an oxidation potential of 1.92 volts. A third preferred cross-linking agent is 4,4'-dihydroxy-benzophenone, which has an oxidation potential of 1.78 volts. Another useful cross-linking agent is 15 2,4-dihydroxybenzophenone.

The curable fluoroelastomer composition also contains a metal compound composed of a divalent metal oxide or hydroxide, such as the oxides or hydroxides of magnesium, zinc, calcium or lead; or a 20 mixture of the oxide and/or hydroxide with a metal salt of a weak acid, for example a mixture containing about 1-20 percent by weight of the metal salt. Among the useful metal salts of weak acids are barium-, sodium-, potassium-, lead-, and 25 calcium-/stearate, -benzoate, -carbonate, -oxalate, and -phosphite. The amount of the metal compound added generally is about 1-15 parts by weight per 100 parts of fluoroelastomer, about 2-10 parts being preferred. The metal compound concentration to some extent affects the rate of cure, and below the 30 preferred range the cure rate is decreased. Above the preferred range, the elastic properties of a cured fluoroelastomer are gradually impaired and it is, therefore, advantageous not to exceed the 35 preferred range of the metal compound.

The metal compound serves a dual purpose. It absorbs certain gaseous and acidic materials which are evolved during vulcanization and can chemically attack and weaken the fluoroelastomer. It also provides a long term aging stability. The metal oxide can be compounded with a fluoroelastomer stock either free or as a metal oxide complex or chelate with organic complexing agents and ligands, such as cyclic polyethers, amines, phosphines, ketones, alcohols, phenols, or carboxylic acids.

In preparing the fluoroelastomer to be used in the present composition, it is preferred that the reaction mixture of monomer components also contains a free-radical initiator, and the copolymer-forming reaction is carried out as a free radical emulsion polymerization reaction. Among the most useful free-radical initiators to use in such a reaction are ammonium persulfate, sodium persulfate, potassium persulfate, or a mixture of two or more such compounds. Also useful are other water-soluble inorganic peroxide compounds, for example sodium, potassium, and ammonium perphosphates, perborates, and percarbonates. The initiator can be used in combination with a reducing agent such as sodium, potassium, or ammonium sulfite, bisulfite, metabisulfite, hyposulfite, thiosulfate, phosphite, or hypophosphite, or in combination with a ferrous, cuprous, or silver salt, or other easily oxidized metal compound. Known organic free-radical initiators can also be used, preferably in combination with a suitable surfactant such as sodium lauryl sulfate or ammonium perfluorooctanoate. The surfactant can be selected from those known to be useful in the manufacture of fluoroelastomer. A surfactant can of course also be present when using

an inorganic initiator. A suitable known chain transfer agent can also be present during the emulsion polymerization reaction, but in many cases this is not preferred.

5 After completion of the preferred emulsion polymerization reaction, the copolymer can be isolated from the resulting polymer latex by known methods, for example by coagulation by adding an electrolyte or by freezing, followed by centrifuging
10 or filtering and then drying the copolymer.

The copolymer-forming reaction can also be carried out in bulk, or in an organic liquid containing an organic free-radical initiator. It is usually preferred that none of the organic liquid
15 present is a chain transfer agent.

During preparation of the copolymer, the reaction mixture is preferably heated in a reactor which has been flushed with an inert gas at about 50°C-130°C. under superatmospheric pressure, for
20 example under a pressure of about $7\text{-}140 \text{ kg/cm}^2$, preferably about $35\text{-}105 \text{ kg/cm}^2$. In some of the most useful procedures, the polymerization is carried out as a continuous process and the reaction mixture has an average residence time in the reactor of about
25 5 to 30 minutes in some cases and up to 2 or 3 hours in others. Residence time can be calculated by dividing the reactor volume by the volume of latex produced per hour.

The fluoroelastomer used in the process of
30 this invention in the majority of cases will have an inherent viscosity of about 0.01 or higher, with special preference for an inherent viscosity of about 0.2-1.2. Inherent viscosity of some of the fluoroelastomers can be measured at 30°C. at a
35 copolymer concentration of 0.1% by weight in a

solvent composed of 87% by volume of tetrahydrofuran and 13% by volume of N,N-dimethylformamide.

The following examples in which all parts are by weight unless otherwise specified are

5 illustrative of the invention.

Examples 1-8

- A composition of the present invention is prepared by blending the following ingredients on a two-roll rubber mill: 100 parts fluoroelastomer A (a
- 10 35/34/29/2 wt% vinylidene fluoride/hexafluoropropylene/tetrafluoroethylene/4-bromo-3,3,4,4-tetrafluorobutene-1 tetrapolymer having a Mooney viscosity (ML-10 at 121°C) of about 60, 30 parts carbon black, 3 parts high activity magnesium
- 15 oxide, 6 parts calcium hydroxide, 4 parts vulcanization accelerator [which is composed of 1 part benzyltriphenylphosphonium chloride dispersed in 2 parts of 60/40 vinylidene fluoride/hexafluoropropylene dipolymer with ML-10 at
- 20 100°C of about 52], 6 parts cross-linking agent [which is composed of 1 part hexafluoroisopropylidene-bis(4-hydroxybenzene) dispersed in 1 part of the dipolymer used in the vulcanization accelerator and amounts of
- 25 1,8-diazabicyclo[5.4.0]undec-7-ene, (DBU), the 2-ethylhexanoic acid salt of DBU, 1,4-diazabicyclo[2.2.2]octane, (DABCO), 1,5-diazabicyclo[4.3.0]non-5-ene, (DBN), and p-dimethylaminopyridine, as shown in Table 1.
- 30 Mooney scorch was measured on freshly milled uncured samples according to ASTM D-1646. Uncured compositions were also used to test cure characteristics with an oscillating disc rheometer (Micro ODR) according to ASTM D-2084. The cure
- 35 states obtained at 177°C and 193°C are shown in the

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tables as $M_H - M_L$ in N·m where M_H and M_L represent the highest and lowest torque readings, respectively. The value t_s 0.2 represents the time from the beginning of the test to a torque increase of 0.2 N·m from M_L . The time in minutes to reach 5 50% and 90% cure state are represented by t_c 50 and t_c 90.

Dumbbells for stress/strain measurement and O-rings for compression set measurement were prepared 10 by compression molding at 177°C at a total force of 4 MN/m² of mold area as described in ASTM D-412 and ASTM D-395, Method B. The compression molded samples were postcured for 24 hrs. at 232°C in a circulating air oven. Modulus, tensile strength and elongation 15 of the press and oven-cured samples were determined at room temperature according to ASTM D-412. Compression set was measured as described in ASTM D-395, Method B.

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TABLE I

<u>Sample</u>	<u>Control</u>	1	2	3	4	5	6	7	8
Fluoropolymer A	100	100	100	100	100	100	100	100	100
MT (N908) Carbon Black	30	30	30	30	30	30	30	30	30
Magnesium Oxide	3	3	3	3	3	3	3	3	3
Calcium hydroxide	6	6	6	6	6	6	6	6	6
Vulcanization accelerator	4	4	4	4	4	4	4	4	4
Cross-linking agent	6	6	6	6	6	6	6	6	6
DBU	-	0.10	0.20	-	-	-	-	-	-
DBU 2-ethylhexanoic acid salt	-	-	-	0.30	0.60	-	-	-	-
DABCO	-	-	-	-	-	0.22	-	-	-
DBN	-	-	-	-	-	-	0.25	-	-
p-dimethylaminopyridine	-	-	-	-	-	-	-	0.12	0.37
<u>Mooney Scorch (MS/121°C)</u>									
Minimum	58	57.5	58.5	73	74	64	59	64	67
Time to 5 point rise (min)	11.5	11	14.6	11	4.8	25	11.8	10	4.8
Time to 10 point rise (min)	22	29	16.8	12.5	5.2	33	13.3	13.5	5.7
<u>Micro ODR (1° Arc), 24 min/177°C</u>									
M _H -M _L (N·m)	4.70	5.60	5.67	-	-	4.92	5.22	3.07	2.73
t _s 0.2, (min)	5.4	3.1	2.4	-	-	2.9	2.3	3.5	1.6
t _c 50, (min)	9.7	4.2	3.2	-	-	4.4	3.9	5.9	2.7
t _c 90, (min)	12.6	5.1	4.0	-	-	5.4	6.1	8.7	4.5

TABLE I (continued)

<u>Sample</u>	<u>Control</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>
<u>Micro ODR (1° Arc), 12 min/193°C</u>									
M _H -M _L (N·m)	4.24	5.31	5.26	-	-	-	-	-	-
t _s 0.2, (min)	3.1	1.9	1.5	-	-	-	-	-	-
t _c 50, (min)	4.2	2.5	1.9	-	-	-	-	-	-
t _c 90, (min)	5.1	3.1	2.5	-	-	-	-	-	-
<u>Micro ODR (1° Arc), 12 min/177°C</u>									
M _H -M _L (N·m)	-	-	5.27	5.25	-	-	-	-	-
t _s 0.2, (min)	-	-	2.2	1.4	-	-	-	-	-
t _c 50, (min)	-	-	3.1	1.9	-	-	-	-	-
t _c 90, (min)	-	-	4.0	2.6	-	-	-	-	-

Stress/Strain

1008 Modulus, MPa	9.3	10.2	10.9	12.6	13.8	9.0	11.8	9.0	9.7
Tensile Strength at break, MPa	15.2	17.1	13.9	14.1	14.5	14.7	15.5	12.2	11.4
Elongation at break, %	180	170	130	110	105	170	135	125	110
Compression Set Method (B) 2.54 cm x 0.353 cm o-rings									
70 hr at 200°C, %	37	29	33	37	40	46	32	40	46
70 hr at 232°C, %	62	63	60	69	72	80	71	74	78

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Examples 9-10

The compositions of Examples 9-10 were prepared as described above in Examples 1-8 but using the ingredients shown in Table II below in the amounts indicated.

5 Fluoropolymer B is a 55/10/34.8/1.2 vinylidene fluoride/tetrafluoroethylene/perfluoromethyl perfluorovinyl ether/4-bromo-3,3,4,4-tetrafluorobutene-1 tetrapolymer having a Mooney viscosity (ML-10 at 121°C) of approximately 90.

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TABLE II

		<u>Controls</u>	<u>9</u>	<u>10</u>
	<u>Sample</u>			
	Fluoropolymer B	100 100	100 100	
5	MT (N908) Carbon Black	30 30	30 30	
	Magnesium Oxide	3 3	3 3	
	Calcium hydroxide	10 10	10 10	
	Vulcanization accelerator	3 4	3 4	
	Cross-linking agent	4 6	4 6	
10	DBU 2-ethylhexanoic acid salt	- -	0.20 0.20	
	<u>Mooney Scorch (MS/121°C)</u>			
	Minimum	60 57	66 61.5	
	Time to 5 point rise (min)	26.5 45	12.3 14.5	
	Time to 10 point rise (min)	32 -	13.8 17	
15	<u>Micro ODR (1° Arc), 30 min/149°C</u>			
	$M_H - M_L$ (N·m)	3.31 3.93	3.19 4.12	
	t_s 0.2, (min)	8.8 12.8	5.2 6.6	
	t_c 50, (min)	14.0 20.5	8.5 9.8	
	t_c 90, (min)	22.0 25.0	17.8 18.0	
20	Press Cure, minutes at 149°C	30 30	10 10	
	Oven Step-cure	Heated for 1 hour at 100°C, then Heated for 1 hour at 121°C, then Heated for 1 hour at 149°C, then Heated for 1 hour at 177°C, then Heated for 1 hour at 204°C, and finally		
		Heated for 24 hours at 232°C to cure.		
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TABLE II (cont'd.)

<u>Stress/Strain</u>	<u>Controls</u>	<u>9</u>	<u>10</u>
100% Modulus, MPa	7.9	9.0	8.5
Tensile Strength at Break, MPa	13.6	14.2	13.3
5 Elongation at Break, %	165	160	155
Hardness, Durometer A	76	80	78
<u>8 Compression Set Method (B), 2.54 cm x 0.353 cm O-rings</u>			
70 hours at 200°C, %	24	22	28
70 hours at 232°C, %	47	54	66

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CLAIMS

1. In a process for rapidly curing a fluoroclastomer composition which comprises mixing and heating:

5 (1) a fluoroclastomer copolymer whose interpolymerized units consist essentially of (a) vinylidene fluoride, (b) at least one other fluorine-containing monomer copolymerizable therewith, said monomer being a compound which 10 contains 2-7 carbon atoms, contains no bromine atom, and contains at least as many fluorine atoms as carbon atoms and (c) contains up to 3 mole percent of units derived from a bromine-containing olefin with the proviso that enough of such units are present to 15 provide at least 0.05 weight percent bromine in the copolymer;

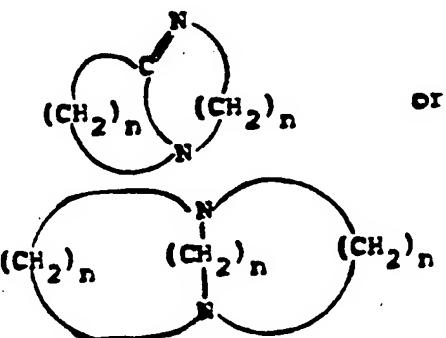
(2) a vulcanization accelerator that is a quaternary phosphonium compound;

20 (3) a cross-linking agent selected from the group consisting of bisphenols or an ammonium or phosphonium salt thereof;

the improvement which comprises adding to the composition

0.1-0.4 parts by weight per hundred parts 25 fluoroclastomer of (a) a dialkylaminopyridine wherein the alkyl groups independently contains 1-5 carbon atoms or (b) a diazabicyclo compound of the formula

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where n is 2-8 or

0.2-0.8 parts by weight per hundred parts
fluoroelastomer of a carboxylic acid salt of (a) or
(b).

5 2. A process of Claim 1 wherein the
diazabicyclo compound is 1,5-diazabicyclo
[3,2,0]non-5-ene.

10 3. A process of Claim 1 wherein the
diazabicyclo compound is 1,4-diazabicyclo-
[2,2,2]octane.

4. A process of Claim 1 wherein the
diazabicyclo compound is
1,8-diazabicyclo[5,4,0]undec-7-ene.

15 5. A process of Claim 1 wherein the
diazabicyclo compound is the 2-ethylhexanoic acid
salt of 1,8-diazabicyclo[5.4.0]undec-7-ene.

6. A process of Claim 1 wherein the
dialkylaminopyridine is dimethylaminopyridine.

20 7. A process of Claim 1 wherein a metal
compound which is divalent metal oxide or divalent
metal hydroxide is added to the mixture in amounts of
from about 1-20 percent based on the weight of the
fluoroelastomer copolymer.

25 8. A process of Claim 1 wherein the
fluorine-containing monomer contains units derived
from a perfluoroalkyl perfluorovinyl ether wherein
the alkyl group contains 1-5 carbon atoms.

9. In a process for rapidly curing a
fluoroelastomer composition which comprises mixing
30 and heating to curing temperatures

(a) a copolymer whose interpolymerized
units consist essentially of (a) 30-60 weight percent
vinylidene fluoride, (b) 20-50 weight percent
hexafluoropropylene and 3-35 weight percent
35 tetrafluoroethylene (c) up to 3 mole percent of
4-bromo-3,3,4,4-tetrafluorobutene-1;

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(b) 0.6-2 parts by weight per hundred parts copolymer of the vulcanization accelerator benzyltriphenylphosphonium chloride;

(c) 1.5-4 parts by weight per hundred parts 5 copolymer of the cross-linking agent hexafluoropropylidene-bis-(4-hydroxybenzene); the improvement which comprises adding 0.1-0.4 parts by weight per hundred parts fluoroelastomer of 1,8-diazabicyclo[5.4.0]undec-7-ene.

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